(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 654 441 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
26.04.2000 Bulletin 2000/17

(51) Int. Cl.[7]: **C01B 17/56**

(21) Application number: **94110206.3**

(22) Date of filing: **30.06.1994**

(54) **Process for purifying sulfur oxides-containing gas**

Verfahren zur Reinigung von Schwefeldioxid enthaltendem Gas

Procédé pour la purification d'un gaz contenant des dioxides de soufre

(84) Designated Contracting States:
DE NL

(30) Priority: **16.11.1993 JP 28684593**

(43) Date of publication of application:
24.05.1995 Bulletin 1995/21

(73) Proprietor:
SUMITOMO HEAVY INDUSTRIES, LTD.
Tokyo (JP)

(72) Inventors:
- **Watanabe, Teruo**
  Ushiku-shi (JP)
- **Tanaka, Hiromi**
  Abiko-shi (JP)
- **Kobayashi, Kouji**
  Ichihara-shi (JP)

(74) Representative:
Henkel, Feiler, Hänzel
Möhlstrasse 37
81675 München (DE)

(56) References cited:
DE-B- 1 061 304
DE-C- 706 737
DE-C- 751 907
US-A- 1 821 064

EP 0 654 441 B1

Printed by Xerox (UK) Business Services
2.16.7 (HRS)/3.6

Description

BACKGROUND OF THE INVENTION

1) Field of the Invention

[0001] The present invention relates to a process for purifying a gas containing sulfur dioxide in high concentration.

2) Related Prior Art

[0002] A gas containing sulfur oxides (SO_x) at a high concentration is obtained by contacting a flue gas with a carbonaceous adsorbent, thereby removing sulfur oxides or sulfur oxides and nitrogen oxides from the flue gas and regenerating the sulfur oxides-adsorbed carbonaceous adsorbent with heating. Elemental sulfur is recovered from the gas containing SO_x at a high concentration, for example, by a reduction treatment of the gas according to Claus process. In case of a flue gas from combustion of fuel coal, the gas containing SO_x at a high concentration also contains halides originating from sea water sprayed over fuel coal to prevent coal dust generation before combustion. Furthermore, when ammonia is added to a flue gas to conduct removal of nitrogen oxides therefrom, most of ammonia adsorbed on the carbonaceous adsorbent, which also works as a catalyst for removing nitrogen oxides, is decomposed to a nitrogen gas during the regeneration of the adsorbed carbonaceous adsorbent with heating, whereas undecomposed ammonia is contained in the gas containing SO_x at a high concentration.

[0003] These impurities such as halides and ammonia give rise to corrosion of the Claus process apparatus or poisoning of a reducing catalyst in the reactor of the Claus process apparatus, resulting in frequent shutdown of the Claus process apparatus. It is thus necessary to remove these impurities, thereby purifying a flue gas containing SO_x at a high concentration before the flue gas is passed through the Claus process apparatus.

[0004] It has been proposed to purify a gas containing SO_x at a high concentration by leading the gas at a temperature of 200°C or higher to a single washing column and cooling and washing the gas with recirculating water sprayed into the washing column at the upper part, thereby removing impurities such as halides and ammonia (JP-B-5-21008). However, the proposed process has such problems that the impurities such as halides and ammonia are gradually absorbed and accumulated in the recirculating water, lowering the washing efficiency with time, and in order to suppress the lowering of washing efficiency with time it is necessary to supply fresh water, resulting in an increase in the amount of waste water to be treated separately.

[0005] It is also known to purify a gas containing SO_x at a high concentration through a series of two washing columns, where the gas at a temperature of 200°C or higher is quenched in a quenching column, then led to a first washing column and cooled to about 50°C with water supplied by spraying into the first washing column at the upper part; and then the gas is led to a second washing column and cooled to about 40°C or lower with water supplied into the second washing column at the upper part, while discharging the gas containing SO_x at a high concentration and freed from the impurities such as halides and ammonia from the second washing column at the top. In the conventional process for purifying a gas containing SO_x at a high concentration based on the series of two washing column, cooling of the gas is carried out mainly in the first washing column and purification of the gas to remove the impurities is carried out mainly in the second washing column. That is, recirculating water can be used as water to be supplied into the first washing column directed mainly to the cooling, whereas fresh water must be used in the second washing column directed mainly to the gas purification.

[0006] In a dry process SO_x removal treatment or a dry process SO_x-NO_x removal treatment, "no water supply" (which means that the treatment is carried out without any supply of water,) in a target next to no waste water discharge" (which means that the treatment is carried out without any discharge of waste water), and the conventional process requiring fresh water is thus not satisfactory yet, even if purification of the gas can be carried out completely.

[0007] US-A-1,821,064 discloses a process for purifying SO_2 by water washing the SO_2 containing gas in two steps, the first at a temperature of about 40°C, the second at a temperature of about 30°C. The washing water is said to be very efficiently utilised.

[0008] DE-C-706 737 discloses a process for purifying SO_2 containing gases by washing the SO_2 containing gas in two steps. It is suggested to use water as a washing liquid. The outlet temperature of the first step is about 80°C, the outlet temperature of the second step is about 30°C. The gases in the first step are saturated with water vapour. The water vapour condenses in the second step and is there used as washing liquid.

SUMMARY OF THE INVENTION

[0009] An object of the present invention is to provide a process for efficiently removing impurities such as halides and ammonia from a gas containing SO_x at a high concentration without any substantial supply of fresh water.

[0010] According to the present invention, there is provided a process for purifying a gas containing sulfur dioxide at a high concentration, which comprises passing a gas containing sulfur dioxide at a high concentration and sulfur trioxide, halogen compounds, ammonia and other impurities to a first water washing column and then to a second water washing column of a set of two water washing columns connected in series, thereby removing the sulfur trioxide, halogen compounds, ammonia and other impurities therefrom, the first and second water washing columns being provided each with a washing water recycle system, each having an independent pump and only the second water washing column being provided with a cooling system for washing water, while setting an outlet temperature of the gas from the first washing column to a temperature at which the gas can have a maximum water content or a temperature near this temperature and setting an outlet temperature of the gas from the second washing column at least by 20°C lower than the outlet temperature of the gas from the first washing column, so that said first and second washing treatment are carried out without any substantial supply of fresh water from the outside. The impurities include halides, ammonia, ect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

Fig. 1 is an adiabatic cooling diagram showing a gas temperature on the abscissa and a molar humidity on the ordinate.

Fig. 2 is a process flow diagram on the basis of a series of two washing columns according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] According to the present process a gas containing SO_x at a high concentration is fed successively to a first washing column and a second washing column and washed with water in these two washing columns to remove impurities such as halides, ammonia, etc. In this respect, the present process is based on the above-mentioned conventional process using two washing columns.

[0013] A novel point of the present process is to control temperatures of a gas containing SO_x at a high concentration. That is, the present process is characterized by setting an outlet temperature of the gas from the first washing column to a temperature at which the gas can have a maximum water content or a temperature near this temperature and setting an outlet temperature of the gas from the second washing column at least by 20°C lower than the outlet temperature of the gas from the first washing column. The characteristics of the present process will be explained in detail below.

[0014] Fig. 1 is an adiabatic cooling diagram showing a temperature of a gas containing SO_x at a high concentration on the abscissa and a molar humidity on the ordinate, determined by the present inventors.

[0015] In Fig. 1, a molar humidity of a gas containing SO_x at a high concentration at 200°C is 0.424 moles H_2O/mole dry air, and when the gas is adiabatically cooled to lower the temperature of the gas, the molar humidity is increased, and a maximum molar humidity (0.552 moles H_2O/mole dry air) can be obtained at 75°C, where the gas can have a maximum water content. When the gas is further adiabatically cooled from 75°C to a lower temperature, the molar humidity is abruptly lowered contrary to expectation. For example, the molar humidity at 40°C is 0.018 moles H_2O/mole dry air. That is, by cooling the gas from 75°C to 40°C condensed water is formed in an amount corresponding to a difference ΔH_1 between the molar humidity at 75°C (0.552 moles H_2O) and the molar humidity at 40°C (0.018 moles H_2O) per mole dry air, that is, ΔH_1 = 0.534 moles, as shown in Fig. 1. That is, when Q_N moles of the gas is adiabatically cooled, 0.534 x Q_N moles of condensed water will be formed. By setting an outlet temperature of the gas from the first washing column and an outlet temperature of the gas from the second washing column to the above-mentioned conditions, as a large amount of condensed water as 0.534 x Q_N moles can be formed and thus can be used as fresh water in the second washing column. That is, the washing treatment can be carried out without any substantial supply of fresh water from the outside.

[0016] When the outlet temperature of the gas is set to 50°C in the first washing column and that from the second washing column to 40°C, as in the conventional two-column type system, on the other hand, condensed water is formed only in an amount corresponding to a difference between the molar humidity at 50°C (0.14 moles H_2O) and the molar humidity at 40°C (0.018 moles H_2O) per mole dry air, that is, ΔH_2 = 0.122 moles. Then, when Q_N moles of the gas is adiabatically cooled, only as a small amount of condensed water as 0.122 x Q_N moles will be formed. Thus, it is apparent to supply fresh water to the second washing column from the outside.

[0017] The present inventors have found that when the outlet temperature of the gas from the first washing column is about 60°C, only substantially cooling of the gas is carried out in the first washing column without washing the gas, whereas when it was set to 75°C, as in the present invention, washing of the gas can be carried out in the second washing column with efficient removal of impurities such as halides and ammonia.

[0018] In the foregoing, explanation has been made, referring to the outlet temperature of the gas from the first washing column set to 75°C and the outlet temperature of the gas from the second washing column set to 40°C. The object of the present invention can be attained by setting the outlet temperature of the gas from the first washing column to a temperature at which the gas can have a maximum water content or a temperature near this temperature and setting the outlet temperature of the gas from the second washing column at least by 20°C lower than the outlet temperature of the gas from the first washing column.

[0019] The outlet temperature of the gas from the first washing column is preferably 65° to 90°C, more preferably 70° to 80°C, which is selected according to the humidity of a gas containing SO_x at a high concentration to be fed to the first washing column, and the outlet temperature of the gas from the second washing column is preferably not higher than 50°C, more preferably not higher than 40°C. It is needless to say to select the outlet temperature of the gas from the second washing column to be at least by 20°C lower than the outlet temperature of the gas from the first washing column.

PREFERRED EMBODIMENTS OF THE INVENTION

[0020] The present invention will be explained in detail below, referring Example of the present invention and Fig. 2.

Example

[0021] A gas containing SO_x at a high concentration obtained by contacting a flue gas with a carbonaceous adsorbent to remove SO_x and NO_x and regenerating the SO_x-adsorbed carbonaceous adsorbent with heating had the following composition:

SO_2	18.9% by volume
SO_3	3.5 ppm
HCl	1.0 g/Nm^3
HF	0.170 g/Nm^3
NH_3	6 ppm
O_2	0.9% by volume
CO_2	25.4% by volume
H_2O	42.4% by volume

[0022] The gas at 214°C was led to a quench column 1, quenched to 78°C with water sprayed into the quench column 1, and led to the lower zone of a first washing column 2. Recirculating water was sprayed into the upper zone of the first washing column 2 from a first recirculating water tank 3 by a first recirculation pump 4, and the gas was further cooled to remove halides such as HCl, HF, etc. and ammonia by washing with the recirculating water.

[0023] In the present invention cooling of the gas in the first washing column 2 must be carried out so that the gas can have a maximum water content, while avoiding supercooling. Thus, the outlet temperature of the gas from the first washing column 2 was made to be 70° - 75°C by setting a ratio of the recirculating water to the gas (L/G) to 5 - 10 ℓ/Nm^3 and the temperature of the recirculating water to 70° - 75°C. Control of the outlet temperature of the gas from the first washing column 2 was carried out by detecting temperature by a temperature sensor 5 provided in the gas line between the first washing column 2 and a second washing column 7, and adjusting the rate of recirculating water to the first washing column 2 by a controller 6 interlocked with the temperature sensor 5 and the first recirculating pump 4.

[0024] The gas at 70° - 75°C from the first washing column was led into the lower zone of the second washing column. Recirculating water was sprayed into the upper zone of the second washing column 7 from a second recirculating water tank 8 by a second recirculation pump 9 after being cooled through a recirculating water cooler 10, whereby the gas was cooled and the halides such as HCl, HF, etc. and ammonia were removed by the washing.

[0025] In the second washing column 7, the gas was cooled down to 40°C, and thus condensed water was formed therein in an amount corresponding to a difference between a molar humidity at 70° - 75°C and that at 40°C, and it was found not necessary to supply fresh water to the recirculating water in the second washing column 7.

[0026] Purified gas from the second washing column 7 had the following composition. Halides and ammonia were completely removed from the gas.

SO_2	18.9% by volume
SO_3	less than 1 ppm
HCl	0.001 g/Nm^3 (percent removal: 99.9%)
HF	0.006 g/Nm^3 (percent removal: 96.5%)
NH_3	less than 1 ppm (percent removals: 83.3%)
O_2	0.7% by volume
CO_2	25.5% by volume
H_2O	8.7% by volume

[0027] As described above, impurities such as halides and ammonia could be efficiently removed from a gas containing SO_x at a high concentration without any substantial addition of fresh water by controlling the outlet temperatures of the gas from the first washing column and the second washing column to specific temperatures, respectively.

Claims

1. A process for purifying a gas containing sulfur dioxide at a high concentration, which comprises passing a gas containing sulfur dioxide at a high concentration and sulfur trioxide, halogen compounds, ammonia and other impurities to a first water washing column and then to a second water washing column of a set of two water washing columns connected in series, thereby removing the sulfur trioxide, halogen compounds, ammonia and other impurities therefrom, the first and second water washing columns being provided each with a washing water recycle system, each having an independent pump and only the second water washing column being provided with a cooling system for washing water, while setting an outlet temperature of the gas from the first washing column to a temperature at which the gas can have a maximum water content or a temperature near this temperature and setting an outlet temperature of the gas from the second washing column at least by

20°C lower than the outlet temperature of the gas from the first washing column, so that said first and second washing treatment are carried out without any substantial supply of fresh water from the outside.

2. A process according to Claim 1, wherein the outlet temperature of the gas from the first washing column is set to 65° - 90°C, and the outlet temperature of the gas from the second washing column is set to not higher than 50°C, while keeping the outlet temperature of the gas from the second washing column at least by 20°C lower than the outlet temperature of the gas from the first washing column.

Patentansprüche

1. Verfahren zum Reinigen eines Schwefeldioxid in hoher Konzentration enthaltenden Gases durch Hindurchleiten eines Schwefeldioxid in hoher Konzentration sowie Schwefeltrioxid, Halogenverbindungen, Ammoniak und sonstige Verunreinigungen enthaltenden Gases durch eine erste Wasserwaschsäule und anschließend eine zweite Wasserwaschsäule in einem in Reihe geschalteten Satz von zwei Wasserwaschsäulen zur Entfernung des Schwefeltrioxids, der Halogenverbindungen, des Ammoniaks und der sonstigen Verunreinigungen (aus diesem), wobei die ersten und zweiten Wasserwaschsäulen jeweils mit einem Waschwasserrückführsystem ausgestattet sind, jeweils eine unabhängige Pumpe aufweisen und lediglich die zweite Wasserwaschsäule ein Kühlsystem für das Waschwasser aufweist, wobei die Auslaßtemperatur des Gases aus der ersten Waschsäule auf eine Temperatur, bei der das Gas einen maximalen Wassergehalt aufweisen kann, oder eine Temperatur nahe dieser Temperatur und die Auslaßtemperatur des Gases aus der zweiten Waschsäule auf einen Wert mindestens 20 °C unter der Auslaßtemperatur des Gases aus der ersten Waschsäule eingestellt werden, so daß die ersten und zweiten Waschbehandlungen praktisch ohne Zufuhr von Frischwasser von außen her durchgeführt werden können.

2. Verfahren nach Anspruch 1, wobei die Auslaßtemperatur des Gases aus der ersten Waschsäule 65° bis 90°C und die Auslaßtemperatur des Gases aus der zweiten Waschsäule auf nicht mehr als 50 °C eingestellt werden und wobei die Auslaßtemperatur des Gases aus der zweiten Waschsäule mindestens 20 °C unter der Auslaßtemperatur des Gases aus der ersten Waschsäule gehalten wird.

Revendications

1. Procédé pour purifier un gaz contenant du dioxyde de soufre en une haute concentration, qui comprend les étapes consistant à faire passer un gaz contenant du dioxyde de soufre en une haute concentration et du trioxyde de soufre, des composés halogénés, de l'ammoniac et d'autres impuretés à une première colonne de lavage à l'eau puis à une deuxième colonne de lavage à l'eau d'un ensemble de deux colonnes de lavage à l'eau raccordées en série, ce qui permet d'en éliminer le trioxyde de soufre, les composés halogénés, l'ammoniac et les autres impuretés, les première et deuxième colonnes de lavage à l'eau étant chacune dotées d'un système de recyclage de l'eau de lavage, ayant chacune une pompe indépendante, et seule la deuxième colonne de lavage à l'eau étant dotée d'un système de refroidissement pour l'eau de lavage, tout en réglant la température de sortie du gaz de la première colonne de lavage à une température à laquelle le gaz peut avoir une teneur en eau maximale, ou à une température proche de cette température, et en réglant la température de sortie du gaz de la deuxième colonne de lavage à au moins 20 °C en dessous de la température de sortie du gaz de la première colonne de lavage, de sorte que lesdits premier et second traitements de lavage sont mis en oeuvre sans aucun apport substantiel d'eau fraîche de l'extérieur.

2. Procédé selon la revendication 1, dans lequel la température de sortie du gaz de la première colonne de lavage est réglée à 65 à 90°C et la température de sortie du gaz de la deuxième colonne de lavage est réglée à pas plus de 50 °C, tout en maintenant la température de sortie du gaz de la deuxième colonne de lavage à au moins 20 °C en dessous de la température de sortie du gaz de la première colonne de lavage.

FIG. 1

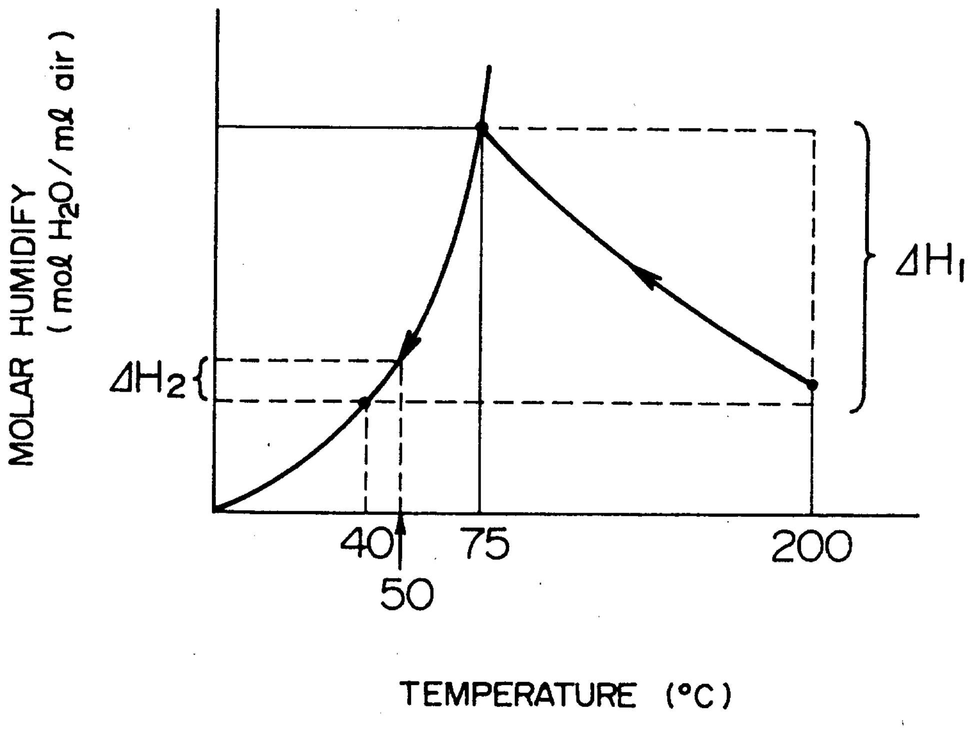
MOLAR HUMIDIFY
(mol H2O / ml air)
ΔH1
ΔH2
40
50
75
200
TEMPERATURE (°C)

FIG. 2